



## Ethanollic Mangifera Indica Leaves Extract as Green Corrosion Inhibitor

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### ARTICLE INFO

#### Article history:

Received 6 October 2022  
Received in revised form 7 January 2023  
Accepted 29 January 2023  
Available online 20 February 2023

#### Keywords:

Organic inhibitor; Mango leaves;  
Copper; Corrosion

### ABSTRACT

Mangifera indica (MI) or mango leaf as a green corrosion inhibitor for copper has been studied. The MI was extracted in ethanol solvent and prepared at different concentrations of 0, 0.4, 0.6 and 0.8 mg/ml in 1 M HCl solutions to imitate the corrosive environment. The as-prepared MI extract analyzed by UV-Vis Spectrophotometer shows a shoulder peak at about 370 nm, resulting from the  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  electronic transition of aromatic C=C and carbonyl (C=O) functional groups. A Fourier transform infrared spectroscopy (FTIR) found that the MI extract exhibits aromatic C=C, C=O groups of phenolic compounds, C-OH, and C-O stretching vibrations. The electrochemical impedance spectroscopy (EIS) and Tafel plot analysis evaluate that the optimum corrosion inhibition of copper was achieved at 0.6 mg/ml concentration. The result is supported by a positive shift in the corrosion potential,  $E_{corr}$ , lower corrosion current,  $I_{corr}$  and corrosion rate (CR) at -0.233 V, 4.39  $\mu\text{A}/\text{cm}^2$  and 0.05 mm/yr, respectively. The surface morphology of the copper substrate after the corrosion test evaluated using metallurgical microscopy shows tremendous corrosion inhibition due to the adsorption of the molecules from the MI extracts.

## 1. Introduction

The extraction of green materials such as seeds and leaves was actively used by people worldwide [1]. In ancient years, Mangifera Indica (MI) leaves have been used as a traditional herbal medicine in many Asian countries. Nowadays, MI has been studied as a green corrosion inhibitor for metallic materials. It was reported that the addition of 1.0 mg/ml MI extracts in 1M HCl managed to mitigate corrosion and increase inhibition efficiency for iron [2]. It is attributed to the mixed inhibition effects of MI that caused both the anodic and cathodic branches to migrate to low current densities. It was said that the addition of MI extract successfully moved corrosion potential,  $E_{corr}$  marginally towards the cathodic branch [3]. The cathodic hydrogen evolution reaction rate is expected to be the primary emphasis of MI extract [4]. On the other hand, another study reveals the cathodic branch shape in Tafel plots almost stays the same. Still, the anodic branch shape dramatically changes with the addition of MI extract [5]. It indicates that the hydrogen evolution reaction mechanism did not

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<https://doi.org/10.37934/araset.29.3.228234>

change in the presence of MI extract, but the inhibitor molecules' adsorption resulted in a significant change in the mild steel dissolution mechanism.

Another significant property of MI extract is the functional groups that contain many heteroatoms, such as oxygen. The natural existence of the organic compounds in the MI extracts may result in the metal's vacant d-orbital interfering with oxygen atoms' lone-pair electrodes [6]. Therefore, it creates animosity between MI extracting corrosive substances such as chloride ions. In addition, the adsorption of inhibitor molecules is strongly dependent on the metal substance's structure and surface. The inhibitors are adsorbed explicitly onto the metal's surface through polar molecules, thereby forming a protective layer [7]. MI extracts have also become crucial because they are environmentally conscious, non-toxic, readily available, and sustainable.

In the meantime, copper metals are widely used for many applications. It has high thermal conductivity, strength and flexibility. However, it is vulnerable to corrosion since passive film formation on copper surfaces is difficult in highly aggressive environments. Therefore, the addition of an inhibitor would be more beneficial. A previous study reported that organic inhibitor has high inhibition efficiency for copper as compared to inorganic inhibitor [8]. Nonetheless, the inhibition efficiency of various MI extract concentrations on copper might vary. It is expected that the MI extract from different mango leaf sources reported in the literature might have assorted inhibitor molecules.

Thus, the present work studied the effect of ethanolic extracted mango leaf as an organic corrosion inhibitor for copper. Various MI concentrations from 0, 0.4, 0.6 and 0.8 mg/ml were prepared from the local tree and subsequently added to the 1M HCl solution. The corrosion inhibition performance of copper was investigated using electrochemical impedance spectroscopy (EIS) and Tafel polarization analysis. The structural properties of the prepared MI extract were pre-determined using a UV-Visible Spectrophotometer (UV-Vis) followed by Fourier transform infrared spectroscopy (FTIR). The surface morphology of the copper substrates after the immersion test is studied using metallurgical microscopy.

## **2. Methodology**

### *2.1 Materials*

Ethanol 98% (Sigma Aldrich), Acetone (Sigma Aldrich), Hydrochloride Acid 38% (Merck), copper foil (99% purity from Kimberly RD, Hong Kong), sandpaper (grade 600-1000), mango leaves and electrodes (Ag/AgCl as reference and Pt as counter).

### *2.2 Sample Preparations*

Mango leaves were collected and dried at 60 °C in an air oven before being ground. In a 200 mL volumetric flask, 20 g of MI powder were soaked in 98 % ethanol and left overnight at room temperature. The mixture was then filtered and evaporated using rotary evaporation to collect the MI extract. Next, the product undergoes a drying process for 24 hours to obtain the MI extract dried powder. The as-prepared MI extract powder was solubilized with DI water and further characterized using UV-Vis Spectrophotometer (UV-Vis) (Cary, model 5000). The FTIR spectrum of the MI powder was obtained using a Fourier Transform Infrared (FTIR) spectrometer (Perkin Elmer) in the wavenumber range of 4000–500  $\text{cm}^{-1}$ . The MI extract was further characterized for its corrosion inhibition properties in 1 M HCl, using copper specimen as the metal sample. The copper foil was cut into 2.0 × 1.0 cm dimensions for the testing. The scales and oxides from the copper surface were removed using sandpapers at 600, 800 and 1000 grades. Acetone was used to remove the residual

impurities such as oil and grease. The copper foils were dried naturally in the environment and placed in a desiccator before being used. The Electrochemical Impedance Spectroscopy (EIS) and Tafel plots were used for the purpose of evaluating the corrosion performance of the samples. The tests were conducted on three replications using PGSTAT101; Autolab by Metrohm.

### 3. Results

#### 3.1 *Magnifera Indica* (MI) Extract Characterizations

The absorption spectra acquired from UV-Visible spectrophotometer (UV-Vis) confirmed the absorption peaks associated with the MI extract at the wavelength range 240 – 400 nm (Figure 1 (a)). The MI extract exhibits a characteristic peak at approximately 314 nm and a shoulder peak at about 370 nm, resulting from the  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  electronic transition of aromatic C=C and carbonyl C=O functional groups [9,10]. The results are consistent with the MI extract molecules like gallic acid, iriflophenone and Mangiferin [11]. Fourier transform infrared spectroscopy (FTIR) spectrum of the MI extract is shown in Figure 1 (b). The broad absorption band at  $3359\text{ cm}^{-1}$  is attributed to typical O-H stretching vibrations of phenolic compounds and alcohols. Further, the peak at approximately  $1640\text{ cm}^{-1}$  was assigned to carboxylic acid carbonyl (C=O) groups in phenolic compounds and aromatic C=C. Moreover, the peak observed at  $1372$  and  $1238\text{ cm}^{-1}$  correspond to the C-OH and C-O stretching vibrations, respectively. Hence, it can be inferred that the MI extract contains a rich source of phenolic compounds as shown by UV-Vis and FTIR results.

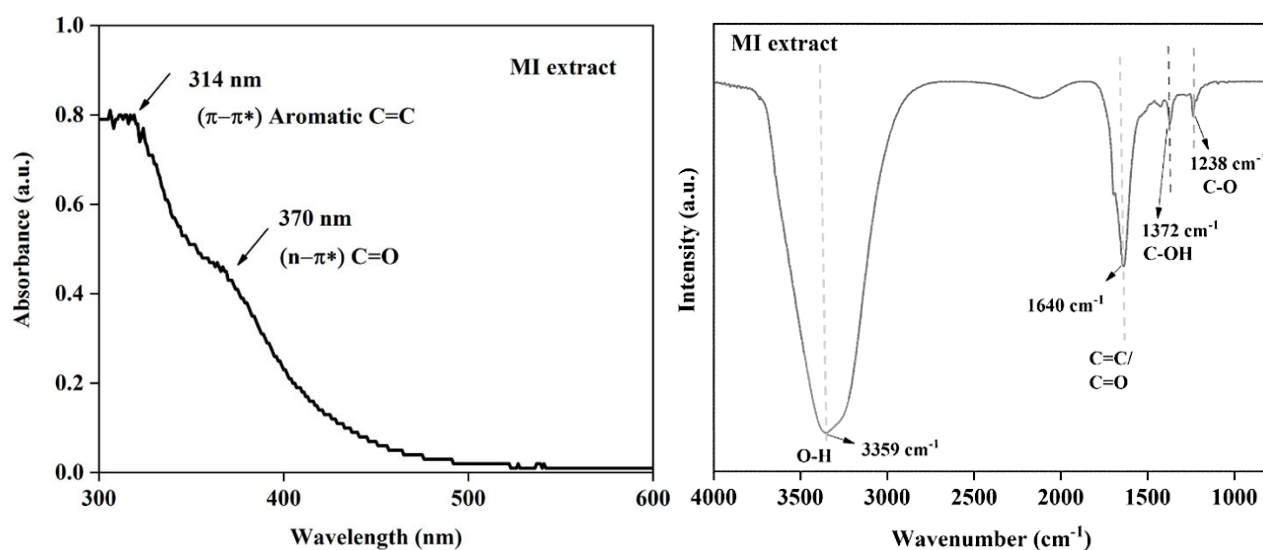


Fig. 1. (a) UV-Visible and (b) FTIR spectra of the as-prepared MI extract

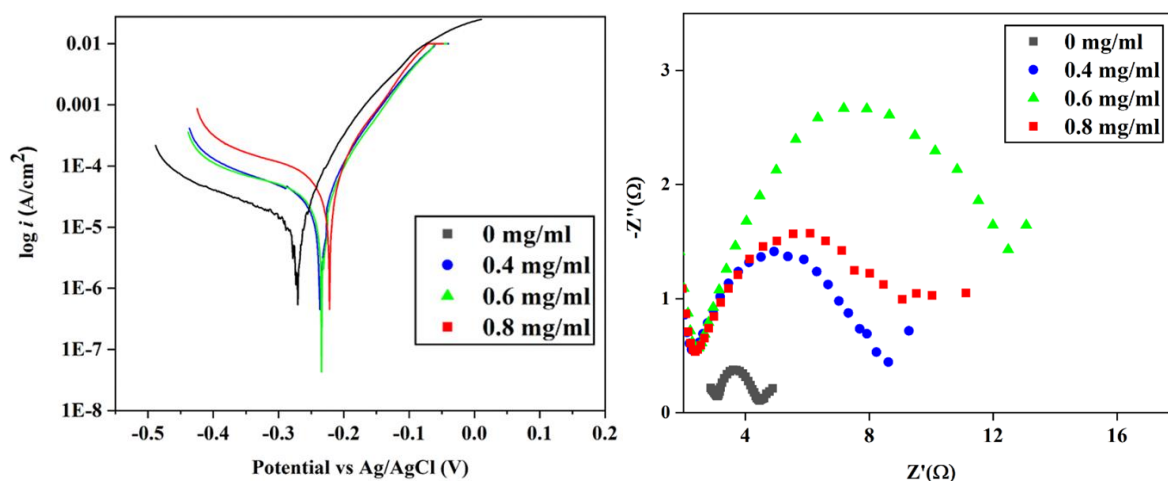
#### 3.2 Corrosion Inhibition Performance

The trend of corrosion inhibition for copper at different MI extract concentrations was observed using electrochemical impedance spectroscopy (EIS). The MI extract at 0, 0.4, 0.6, and 0.8 mg/ml was added to the 1M HCl solution and Nyquist plots were obtained as shown in Figure 2 (a). It is observed that without MI extract (0 mg/ml), the impedance value is smaller than the solution with MI extract. As the concentration of MI extract increases to 0.4 and 0.6 mg/ml, the impedance values also increase. The results are in agreement with the fact that a greater impedance value results in better corrosion inhibition [12]. However, the impedance value slightly decreases as the concentration of MI extract increases to 0.8 mg/ml. A higher concentration of MI extract might cause poor adsorption

and adhesion of the inhibitor molecules since the competition on the copper surface is heightened. Therefore, copper would experience a faster dissolution rate in the corrosive media than its 0.6 mg/ml content.

Figure 2 (b) shows the Tafel plots for MI extract at different concentrations in 1M HCl solution. From the plots, it is observed that the corrosion potential,  $E_{corr}$  for 0.8 mg/ml, is shifted towards a positive direction as compared to 0, 0.4 and 0.6 mg/ml. The  $E_{corr}$  values for the 0, 0.4, 0.6 and 0.8 mg/ml are -0.269, -0.238, -0.233, and -0.220 V, respectively. Meanwhile, the corrosion current,  $I_{corr}$  is found to be 35.21, 23.80, 4.39, and 33.51  $\mu\text{A}/\text{cm}^2$ , respectively. The higher positive value of  $E_{corr}$  and lower value of  $I_{corr}$  denote better corrosion inhibition of sample 0.6 mg/ml. It is worth mentioning that the  $I_{corr}$  for 0.6 mg/ml is approximately eight times of magnitude lower than that of the 0.8 mg/ml, suggesting that the optimum concentration of MI extract is 0.6 mg/ml. At such a lower concentration, it remarkably decreases Cu dissolution due to the adequate content of aromatic rings and carbonyl groups. The functional groups help in the adsorption and adhesion of the molecules onto the copper surface subsequently form a hydrophobic layer. Further addition of the MI extract molecules has drawback effects on the attachment of the molecules. It might be due to the impact of all possible protonated forms, such as oxygen sites for protonation on the copper surface. For confirmation, EIS and Tafel polarization test has been carried out for 1.0 mg/ml MI extract. Interestingly, the result shows a similar trend in which the impedance value decreases and  $E_{corr}$  shifts to the positive direction but  $I_{corr}$  increases, denoting higher degree of copper dissolutions. The result for 1.0 mg/ml is not discuss further here since it exhibits similar outcome with 0.8 mg/ml.

Meanwhile, Table 1 summarizes electrochemical parameters obtained from the Tafel plot analysis. It is observed that the corrosion rate (CR) for 0.6 mg/ml is the lowest at 0.05 mm/yr and the polarization resistance is found to be 928.71  $\Omega$ . The result shows that the MI extract could be an effective corrosion inhibitor at a lower concentration. The existence of heteroatoms in the MI molecules might chelate with copper through an electron sharing mechanism. The vacant orbital of metallic cations may be full of lone pair electrons of heteroatoms like oxygen, thereby improving the corrosion inhibitors. The results also indicate a dense and effective protective film is formed on the copper surface and inhibit the diffusion of  $\text{Cl}^-$  to the copper electrode surface [13-15].



**Fig. 2.** (a) Nyquist plots and (b) Tafel plots of copper immersed in 1M HCl solutions at different MI concentrations

**Table 1**

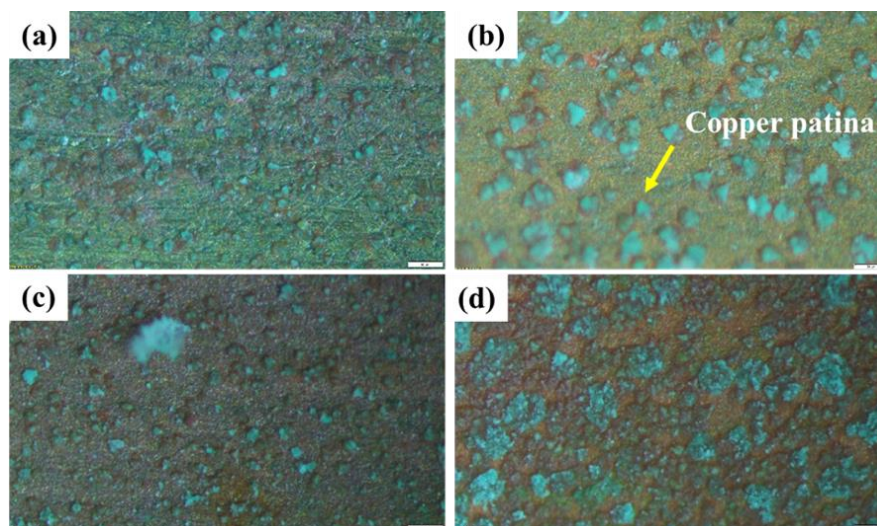
Electrochemical parameters derived from Tafel plots of the samples immersed in 1 M HCl solutions at various MI concentrations

Concentration (mg/ml)	$E_{corr}$ (V)	$I_{corr}$ ( $\mu\text{A}/\text{cm}^2$ )	Corrosion rate (mm/year)	Polarization resistance ( $\Omega$ )
0	-0.269	35.21	3.89	198.21
0.4	-0.238	23.80	0.28	688.05
0.6	-0.233	4.39	0.05	928.71
0.8	-0.220	33.51	0.39	345.1

### 3.3 Surface Study

Metallurgical microscopy at 500x magnification evaluate the surface morphology of copper substrates after the corrosion test. Figure 3 (a) – (d) shows the micrographs of the corroded copper surface with adsorption layers of inhibitor and corrosive product of copper (patina). The morphology revealed that, in the absence of MI extract, the copper surface is highly corroded as shown by the large area of the patina island. However, in the presence of MI extract at 0.6 mg/ml, the patina island becomes smaller, less corroded and has a smoother surface. When the concentration of MI extract increases to 0.8 mg/ml, the surface of copper become more severe.

The type of corrosion seen on the copper surface could be identified as pitting corrosion due to the appearance of corrosion product that spreads almost on all surfaces. Overall, the corrosion inhibition mechanism for 0.6 mg/ml sample can be illustrated by the small and few pitted areas occurs on the copper surface due to good MI antioxidant properties [16]. It is suggested that MI extract could form complex bonds with copper ions and successfully create a thin layer so that the corrosion rate can decrease significantly.



**Fig. 3.** Surface study of copper after corrosion test in 1M HCl solution with (a) 0, (b) 0.4, (c) 0.6, and (d) 0.8 mg/ml MI extract

### 4. Conclusions

The corrosion inhibition of copper in 1M HCl solution containing various loading of MI extract was successfully examined by EIS, Tafel plots and surface analysis. The presence of many active components with aromatic and oxygen-containing functional groups in the extract of MI was shown by Fourier transform infrared spectroscopy (FTIR) and UV-visible spectrophotometry (UV-Vis). The



structural analysis showed that the polyphenols compound represented as hydroxyl and carbonyl functional groups are successfully extracted using ethanol from the MI leaves. The compound has an antioxidant property, which can prevent corrosion of copper by adsorption process. It can be concluded that MI extract at 0.6 mg/ml concentration can prevent rapid deterioration of copper due to the existence of adequate C and O elements in the extracts. The MI extract has proven to behave as mixed type inhibitor which affects both anodic and cathodic reactions rates. It was shown by the decrease in surface damage of copper where smooth layer is formed by the inhibitor especially on the active sites.

### Acknowledgement

The authors would like to acknowledge the funding from Universiti Malaysia Pahang in the form of grant (RDU220311).

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